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Analysis of Dopant Diffusion in Molten Silicon Induced by a Pulsed Excimer Laser

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Dopant diffusion calculations explain well the mechanism of the non-equilibrium incorporation of boron from the silicon surface into the molten silicon induced by a pulsed excimer laser. When a high-power laser causes the melt front to proceed into the substrate faster than 8 m/s, p^+ doped regions are formed only near the surface of the molten region because dopant atoms cannot diffuse sufficiently fast for the junction depth to reach the maximum melt depth.

§1. Introduction

Ultra-shallow junctions have received much attention recently because submicron gate metal-oxide-semiconductor (MOS) transistors require a source and drain whose depth is on the order of 0.1 μm. In order to form such a shallow junction, new doping techniques using a pulsed UV excimer laser have been developed.[1-3] Deutsch *et al.*[1] first reported a laser-doping technique in which a silicon wafer was irradiated in $B(CH_3)_3$ gas by a pulsed ArF excimer laser. A 0.1 μm-deep p^+-n junction was successfully fabricated. We reported the laser-induced melting of pre-deposited impurity doping technique (LIMPID).[4] This technique employs a radio-frequency glow discharge (rf-GD) to deposit a thin dopant film uniformly on a silicon wafer by decomposition of a dopant gas such as B_2H_6 and PH_3, followed by irradiation with a pulsed XeCl-308 nm excimer laser, leading to a superficial melting of the silicon and to dissolution of the dopant. Doping with a concentration as large as 1×10^{21} atoms/cm^3 and with a low resistivity of 15 ohm/□ has been achieved by irradiation with only a single pulse of a laser beam. The p^+-n junction formed by the LIMPID procees has shown an ideal I-V performance with an ideality factor of 1.03.[5]

It seems to be generally believed that in the laser-doping process dopant atoms rapidly and uniformly diffuse from the surface throughout the molten region induced by the laser beam. However, the melting induced by pulsed laser irradiation occurs in conditions of thermodynamic non-equilibrium[6,7] in which the melt front rapidly proceeds into the substrate during irradiation and subsequently moves back to the surface after irradiation. In this paper, we use computer simulation to examine the behavior of dopant diffusion during laser-induced melting. The fitting of calculated results to experimental data provides the diffusion coefficient of boron in molten silicon and the relation between melt depth and junction depth.

§2. Melt behavior of surface region

The usual unidimensional heat-diffusion equation including the melting process was solved analytically[8] in order to obtain the melt behavior of silicon surface region. We assumed that the photon energy was instantaneously converted into heat at the surface because the skin depth is as small as 20 nm at the wavelength of 308 nm. The differential equation for the temperature $T(x, t)$ at time of t and at depth of x is

$$\frac{\mathrm{d}T(x,t)}{\mathrm{d}t}-\frac{\mathrm{d}}{\mathrm{d}x}\left(D\frac{\mathrm{d}T(x,t)}{\mathrm{d}x}\right) = p(x,t)\begin{cases} p_0 & 0<t<\tau \text{ and } x=0 \\ 0 & t>\tau \text{ or } x>0 \end{cases} \tag{1}$$

where $p(x, t)$ is the heat generation rate which has a value of p_0 during laser irradiation. D is the thermal diffusion coefficient which involves the thermal conductivity, specific heat, and the density of silicon. τ is the laser pulse width of 30 ns. We used the values of thermal conductivity and specific heat in solid silicon from the compilation of Goldsmith *et al.*[9] and the value of thermal conductivity and specific heat in molten silicon of Wood and Giles.[6] The solid phase changes to the molten phase when the region at the melting point absorbs the latent heat. The molten region expands and then contracts under the condition in which the sum of thermal energy of the molten region and the solid regions is equal to the absorbed laser energy.

Figure 1 shows the calculated melt front motion of silicon on which transparent SiO_2 (1000 A) and boron (100 A) films were deposited to be used in the LIMPID process. The laser irradiation at an incident energy of 1.0 J/cm^2 melted the silicon surface and the melt front rapidly proceeded into the silicon substrate during irradiation with a laser pulse, and later moved back to the

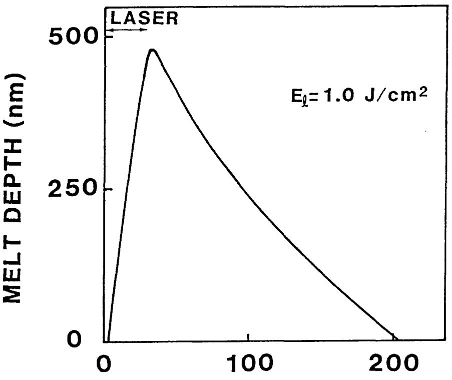

Fig. 1. Melt fornt motion as a function of time for SiO_2 (1000 A) and boron (100 A) deposited Si sample. E_l is the incident laser energy density. The laser-pulse width is 30 ns.

surface. In the laser-doping process, dopant atoms diffuse from the surface into the molten region whose depth varies with time. In order to determine the melt front profile to be used to calculate the dopant profile, we investigated the melt duration at the surface by measuring the high reflectivity phase associated with surface melting[10,11] using an Ar-514.5 nm laser beam as probe light.[5] The deposition of the SiO_2/boron film decreased the reflectivity at the surface from 62% (bare Si) to 42% at 308 nm (anti-reflection effect) and the laser irradiation at 1.0 J/cm^2 melted the surface for 200 ns.

§3. Analysis of dopant profile

The diffusion of dopant in molten silicon occurs with a coefficient on the order of 10^{-4} cm^2/s,[12] while the diffusion coefficient of dopant in solid silicon is as small as 10^{-11} cm^2/s.[13] This allows us to ignore the diffusion of dopant in the solid region during laser treatment. We divided the melt-front profile into N segments by a time interval of Δt. The depth of the melt front at the n^{th} segments is assumed to be $(X_{n-1}+X_n)/2$, where X_n is the depth of the melt front at $(n\times\Delta t)$ s. The melt front thus proceeds into the substrate and returns to the surface in finite steps, and diffusion is stationary in the molten region within a step. For the time interval of Δt, the dopant diffusion equation at the n^{th} segment can be solved by the image method[8] using the profile of the $(n-1)^{\text{th}}$ segment and the boundary planes of the melt front and the surface. The segregation coefficient of boron at the liquid-solid interface was assumed to be 1[14]. The dopant concentration $C(n, x)$ at the n^{th} segment and at x nm is

$x \leq X_m$:

$$C(n,x)=\frac{A}{2\sqrt{\pi D_d \Delta t}}\int_0^{X_m} C(n-1,x')\times\left[\sum_{k=-\infty}^{\infty}\exp\left[-(x-x'-2kX_m)^2/4D_d\Delta t\right]+\sum_{k=-\infty}^{\infty}\exp\left[-(x+x'-2kX_m)/4D_d\Delta t\right]\right]\mathrm{d}x', \tag{2}$$

$x > X_m$:

$$C(n,x)=C(n-1,x),$$

where D_d, Δt, X_m, and A are the diffusion coefficient of the dopant, the time interval of 1 ns, the depth of melt front of $(X_{n-1}+X_n)/2$, and an appropriate normalization factor, respectively. Before laser irradiation, dopant atoms are located at the surface, and the diffusion profile at first step is

$$C(0,x)=\begin{cases} C_0 & \text{at } x=0 \\ 0 & \text{at } x>0 \end{cases} \tag{3}$$

where C_0 is the initial concentration of dopant atoms. The final profile at the first irradiation of a laser beam is obtained by calculating eq. (2) from the first to the N^{th}

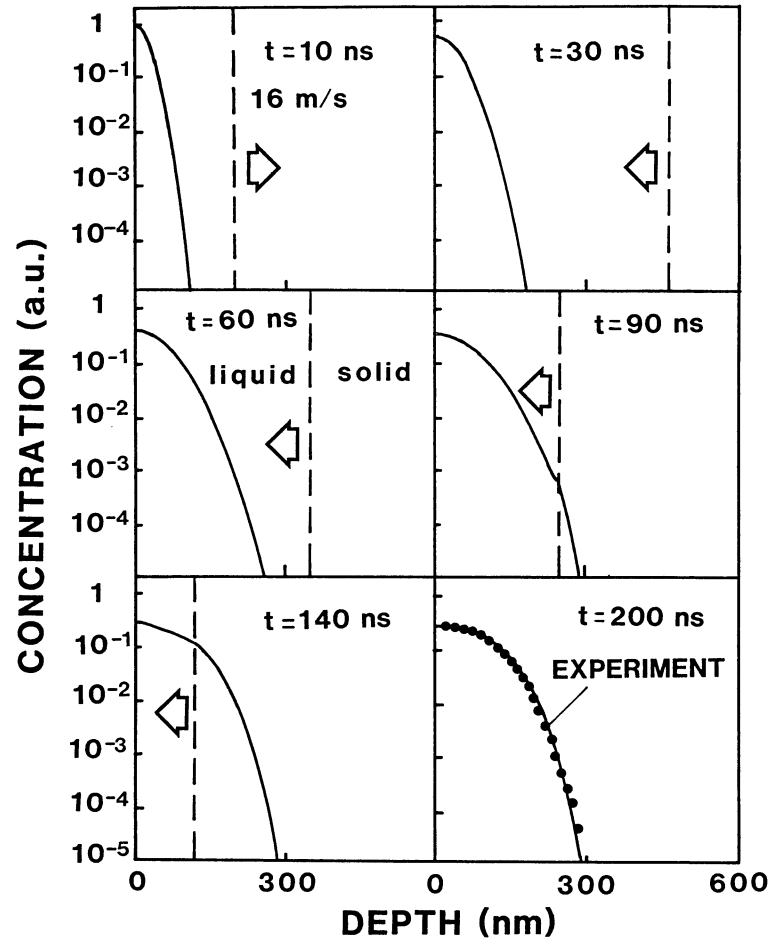

Fig. 2. Calculated boron profiles at various times from surface melt. The melt front proceeds from surface into silicon with a velocity of 16 m/s. The surface melts for 200 ns. SIMS profile at incident laser energy of 1.0 J/cm^2 is also plotted at a time of 200 ns.

segment using the initial condition of eq. (3) and with a melt front whose depth changes at every step. Calculation of the integral between the surface and the melt front in eq. (2) was carried out using steps of 2.5 nm. Components in the summations of the image effect in eq. (2) were ignored when they contributed less than 1% to the profile of $C(n, x)$. Since the diffusion coefficient of the dopant in the laser-doping process is not known well, we calculated dopant profiles varying the parameter D_d in eq. (2) to fit to experimental data.

Since the calculation of the profile is carried out step-by-step with a finite time interval, we can obtain the evolution of dopant profile during melt and solidification. Figure 2 shows the calculated profiles with a diffusion coefficient of 2.5×10^{-4} cm^2/s at different stages of the melt induced by irradiation with a single pulse at 1.0 J/cm^2 and the boron profile obtained by secondary ion mass spectrometry (SIMS). After 10 ns, laser irradiation was continuing and the melt front was proceeding into the substrate. The melt front moved faster than the boron atoms diffused because the velocity of the melt front which can be obtained from Fig. 1 is approximately 16 m/s, which was much larger than that of dopant diffusion. After 30 ns, solidification occurred and the melt front returned toward the surface, while dopant was still diffusing into the molten region. After 90 ns, the melt front came across the dopant profile. The part of the profile which the melt front passed through was frozen in the solid region and the dopant in the molten region was redistributed between the boundary planes of the melt front and the surface. In this way, the characteristic profile for laser doping was formed when solidification was completed at 200 ns. The good agreement between calculation results and SIMS indicates that the dopant profile is formed by a simple diffusion process in molten region. The diffusion coefficient of 2.5×10^{-4} cm^2/s agreed well with the value of boron in molten silicon found by Kodera.[12] The boron profile formed at 1.0 J/cm^2 had a junction depth of 300 nm, which was defined as the depth at a concentration of 1×10^{15} atoms/cm^3 because we used a substrate which had a carrier concentration of about 1×10^{15} atoms/cm^3. The junction depth was smaller than the maximum melt depth of 480 nm, and the p$^+$ layer was formed in the near urface molten region.

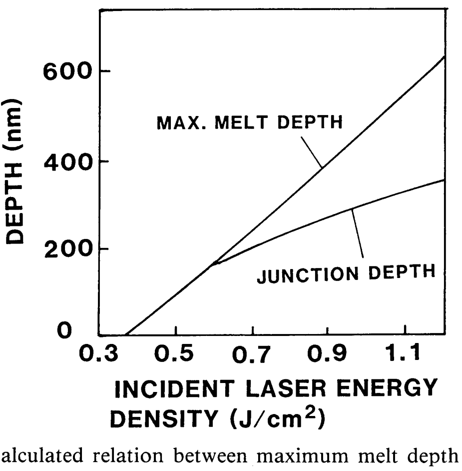

Fig. 3. Calculated relation between maximum melt depth and junction depth in boron doping as a junction of incident laser energy density.

The calculation of the melt front profile and the dopant profile shows us an interesting relation between maximum melt depth and junction depth. Figure 3 shows the dependence of both melt depth and junction depth on incident laser energy. The junction depth increased together with the melt depth below 0.6 J/cm^2 because the velocity of the melt front was slower than 8 m/s and dopant diffused throughout the molten region. On the other hand, the junction is formed in a part of the molten region above a laser energy of 0.6 J/cm^2.

§4. Conclusion

Calculations of dopant diffusion in molten region explain well the pulsed-laser doping process. The dopant profile strongly depends on the melt front profile because diffusion duration decreases as depth proceeds. Matching the experimental and the calculated data provides a diffusion coefficient for boron 2.5×10^{-4} cm^2/s. When a laser pulse at an energy above 0.6 J/cm^2 causes the melt front to proceed into the substrate faster than about 8 m/s, p$^+$ doped regions are formed only near the surface of the molten region because dopant atoms cannot diffuse sufficiently fast for the junction depth to reach the maximum melt depth.

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